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# A mass-balance approach to quantifying the importance of in-stream processes during nutrient transport in a large river catchment

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## Abstract

The importance of riverine processes in the River Swale catchment in Yorkshire, UK, have been assessed during three intensive monitoring campaigns of approximately 100-h duration in the autumn, spring and winter of 1995/1996. This was done by monitoring dissolved silicon, calcium, soluble phosphorus, nitrate, nitrite, ammonium and total phosphorus concentrations at 2-h intervals at the main river and major tributary sites and daily at 15 minor tributaries. These data, together with water discharge data from gauging stations on the main river and major tributaries as well as manual measurements of the minor tributaries, have been used to calculate mass-balances. The difference between the inputs and outputs from the section, enable within-reach losses and gains to be estimated and compared with the water-balance for the river. Dissolved silicon was relatively conservative compared with calcium which did show losses from the river water in the Spring and Autumn, probably associated with precipitation of calcite. Relatively large decreases in soluble phosphorus were found which may be associated with uptake by bed-sediments and riverine flora during conditions of low-flow. Uptake of soluble phosphorus by suspended sediments was also important in a storm event as shown by increases in the mass-balance of particulate phosphorus. Mass-balances for nitrate indicated smaller changes compared with dissolved phosphorus, with losses in the autumn, gains in the spring and little evidence of riverine processes in the winter storm. Ammonium was also lost from the water during all three campaigns but not in sufficient amounts to account for concomitant increases in nitrate or nitrite by nitrification. Exports of soluble reactive phosphorus, total phosphorus and nitrate were calculated for each of the campaigns. The export of total phosphorus was compared with predicted values using suitable export coefficients for different land-use in the UK. The results are consistent, with the export predictions falling in the measured ranges for the catchments. The exports of nitrate were particularly large during the storm event compared with literature data for annual exports. © 1998 Elsevier Science B.V.

*Keywords:* Riverine processes; Catchment; Mass-balance; In-stream

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## 1. Introduction

The role of riverine processes in influencing water quality in large river systems remains uncertain because of problems in applying results from laboratory experiments to conditions found in rivers. Models which include in-stream processes are often validated using optimisation methods to produce agreement with field data and cannot be used to provide an independent evaluation of the processes. This has led to the use of experimental mesocosms or experimental streams to study the mechanism of reactions with sediments, the influences of stream biota on the water chemistry and ecotoxicology of pesticides (Ladle et al., 1977; House et al., 1989; Mitchell, 1994; House and Denison, 1997). These systems represent an intermediate stage between a laboratory scale and studies of river catchments. They are normally restricted to applications where the surface area of the river bed-sediment to the volume ratio is relatively high, e.g. 1–10 $m^{-1}$, so are applicable to small channels rather than large rivers where the ratio is usually lower. With high ratios, interactions of chemicals with the sediments, such as the release of nutrients, will have a greater impact on the overlying water quality.

Scaling results from laboratory studies to large rivers is more difficult. Hence it is not surprising that there remains much uncertainty about the influences of riverine processes on water quality in general. Mass-balance studies can, in principle, provide the necessary information but are notoriously difficult to implement on large rivers. This is because of the need to monitor all inputs in the study section — chemical concentrations and water discharge as well as maintaining a high standard of chemical analysis for unstable determinants. The present study attempts to address this by examining in detail a 55-km reach of the River Swale in Yorkshire in conditions of low river-flow in the autumn, during a low-flow period in the spring and during a major winter storm. The determinants chosen for the study are dissolved phosphorus (soluble reactive and total dissolved SRP and TDP, respectively), total phosphorus (TP), nitrate, nitrite, ammonium as well as dissolved silicon and calcium. The purpose of the research is to provide information about the net effects of riverine processes at different times of the year and provide a bases for more detailed mesocosm studies as appropriate. The work complements other studies of nutrients (e.g. Ainsworth and Goulder, 1998; House and Warwick, 1998; Jarvie et al., 1998; Pattinson et al., 1998) within the context of the Land Ocean Interaction Study (LOIS) described by Leeks and Jarvie (1998).

## 2. Catchment

The study section was between Catterick and near Thornton Manor in the south of the catchment of the River Swale in Yorkshire, UK (see map of catchment). This is a 55-km stretch of river described in detail by House and Warwick (1998). The sampling sites were at the Environmental Agency gauging stations at Catterick and either Crakehill or Leckby (NGR: SE 426 734) as the downstream site, at Bedale Beck (NGR: SE 302 905), River Wiske (SE 375 844) and Cod Beck (NGR: SE 422 766) as well as 15 ungauged minor tributaries (House and Warwick, 1998) with the sampling points chosen as close to the confluence with the main river as practicable.

The River Swale covers a large catchment (1457 $km^2$) encompassing both upland and lowland areas. The river starts in the Pennines in the north of England from a confluence of small soft-water streams but becomes progressively harder water on passage through progressively younger rock from carboniferous limestone to Triassic Mercia mudstone. The upland is dominated by low intensity agriculture and moorland which supports sheep farming and a small amount of dairy farming. In the lowland catchment, south of Catterick, the agriculture is mixed with arable, sheep, cattle and poultry farming and includes urban areas such as the towns of Northallerton and Thirsk. Details of the geography and hydrology of the catchments are given by Jarvie et al. (1997) and Lewis et al. (1997).

## 3. Methods

Three sampling campaigns are reported: (a) 27–31 October 1995 of 100-h, (b) 22–26 February

1996 of 108-h and (c) 25–29 April 1996 of 100-h duration. Automatic water samplers (EPIC model 1011) were programmed to collect 1-l samples at 2-h intervals at the main river sites at Catterick and Leckby (in October 1995) and Crakehill (in February and April 1996) as well as at the major tributary sites (River Wiske and Cod Beck). Bedale Beck and the minor tributaries were visited daily to sample and measure stream-water discharge (stream cross-section and water velocity using an ultra-sonic sensor, SENSA RC2). Samples from the automatic samplers were collected daily, immediately filtered through 0.45 $\mu$m cellulose nitrate membrane and analysed for soluble reactive phosphorus (SRP) by the method of Murphy and Riley (1962). Filtered and unfiltered samples were transported by overnight carrier to the Institute of Freshwater Ecology, River Laboratory and analysed for total dissolved phosphorus (TDP), nitrate, nitrite, ammonium and dissolved silicon by flow-injection analysis (House and Warwick, 1998) and dissolved calcium by EDTA titration (Vogel, 1961). Unfiltered samples were used for total phosphorus (TP) determination (Eisenreich et al., 1975). Prior to the campaigns, nutrient stability tests were done to assess the effects of short sample storage in the automatic samplers and during transit to laboratories (House and Warwick, 1998).

The entire river section between Catterick and Crakehill was surveyed in detail from 18 to 21 June 1996 by walking along the river bank and noting minor inflows, geomorphology of the bed and river width at low-flow, i.e. width at the water line in base-flow conditions and width between the flood banks. Samples of sieved bed-sediment (< 2 mm size), were also taken in each 2-km section and their equilibrium phosphate concentration, $EPC_0$ measured using the method described by House et al. (1995) but using a two-point isotherm. Information on riparian land-use was also noted. A more detailed survey of land use within the River Swale catchment was done using a geographic information system with the Ministry of Agriculture and Fisheries small area statistics data (MAFF, 1992).

After the intensive monitoring in April, four sediment trays (30 cm long, 10 cm wide and 5 cm deep) were placed in the river bed at Leckby and left for 3 months before retrieval. After this time, the trays were immediately transported to the IFE River laboratory and used in fluvarium channel experiments to measure the uptake and release of nutrients in controlled water flow conditions (Zhmud et al., 1997).

The results of the nutrient stability studies have been presented elsewhere (House and Warwick, 1998). In summary, although nitrite showed good stability during 24-h storage, both phosphorus and ammonium were found to be unstable to some extent thus leading to the conclusion that they should be measured as soon after collection from the river as possible. The results of an interlaboratory comparison showed good agreement for phosphorus and nitrate but not ammonium (House and Frickers, 1995).

## 4. Theory

A mass-balance for a river section, $M_t$, may be formulated from knowledge of the water discharge and chemical concentrations as follows:

$$M_t = M_u + \sum_{\text{maj}} M_a + \sum_{\text{min}} M_i + \sum_j m_{\text{net}(j)} \tag{1}$$

where $M_u$ is the mass flowing through the upstream site in a given time interval, $M_a$ and $M_i$ are the mass contributions from the major and minor tributaries, respectively and $m_{\text{net}(j)}$ is the contribution to the budget from riverine processes — designated by the $j$ process. This merely states that the delivery of water and chemicals by a river can be accounted for by the amount entering the section, the contribution of major tributaries and the diffuse inputs entering through drainage ditches — here classified as minor tributaries and the processes occurring during transport which act to remove or add further material. These processes may involve abiotic interactions such as the sorption of dissolved phosphorus to suspended and bed sediments, hydrolysis and dissolution/ precipitation reactions or biologically controlled fluxes such as the uptake of nutrients by plants and denitrification/nitrification reactions. The groundwater or direct inputs, i.e. not included in contributions from minor and major tributaries, of surface or sub-surface contributions, are not explicitly incorporated in the equation but may be assessed from the water-balance for the section. A depletion of water may be attributed to evaporation and seepage of river water to groundwater or a surplus to direct inputs not associated with tributaries. Diffuse inputs are effectively accounted for by the flows from the major and minor tributaries which act to channel drainage waters to the main river.

The individual terms in Eq. (1) may be calculated from the concentration ($c$) and water discharge ($q$), respectively:

$$M_i = \int_0^t c_i(t) q_i(t) dt \approx \sum_i (c_i q_i + c_{i+1} q_{i+1}) \Delta t/2 \tag{2}$$

where $\Delta t$ is the sampling time interval. The same approach can be applied to a water balance for the section, i.e. $c_i = 1$. Hence combining Eq. (1) and Eq. (2) permits an estimate of the net effect of the internal process, $m_{\text{net}}$, in the system.

A major limitation of the approach is that systematic errors in the concentration of the determinants and water discharge produce a mass imbalance which may be interpreted as the effect of internal processes on the water chemistry. The errors may be quantified by defining a mass-balance in time interval, $\Delta t$:

$$R = \left( c_1 q_1 + \sum_i c_i q_i \right) \Delta t \tag{3}$$

and with errors in $c$ and $q$:

$$Re = \left[ (c_1 + c_1 \delta_c)(q_1 + q_1 \delta_q) + \sum_i (c_i + c_i \delta_c)(q_i + q_i \delta_q) \right] \Delta t \tag{4}$$

where the subscript 1 refers to the input to the main river section and the summation is for contributions from the major and minor tributaries. The relative errors in concentration and discharge are included as $\delta_c$ and $\delta_q$, respectively. Expanding Eq. (4), substituting for Eq. (3) and assuming terms with the product $\delta_c \delta_q$ are much less than those containing $\delta_c$ or $\delta_q$ alone, then

$$\frac{(R_e - R)}{R} = \delta_c + \delta_q \tag{5}$$

i.e. the relative error in the mass, $R$, is the sum of the relative errors in both concentration and discharge. The value of $\delta_q$ may be estimated from the water-balance for the section of river, i.e. $\delta_c = 0$, with water volumes replacing the mass terms in Eq. (5).

## 5. Results and discussion

The three campaigns covered a range of river conditions. In October there was no rainfall and the river flow was low with a mean water discharge at the downstream site of 4.7 $m^3$ $s^{-1}$ (range 3.9–5.5 $m^3$ $s^{-1}$). In April, there was little rainfall but the discharge was higher at the downstream site at Crakehill (mean 10.5 $m^3$ $s^{-1}$ and range of 8.5–13.8 $m^3$ $s^{-1}$) with a falling hydrograph. In contrast, the campaign in February followed a wet period and covered a major storm. The hydrographs for the main river sites and River Wiske went through complete hydrograph cycles with well-defined peaks (Fig. 1).

### 5.1. Water mass-balance

The river hydrographs were adjusted for the transit time between Catterick and the other sites. The transit time was estimated between Catterick and the lower Swale site (Leckby or Crakehill) from peaks in the hydrograph from data for the period of the campaign or from the closest peaks prior or after the campaign. The transit times for the major tributaries were estimated from the ratio of their distance from Catterick and the distance between Catterick and the lower Swale site. For mass balance studies, the transit time is not an important consideration as long as the duration of the intensive sampling is much greater than the sampling time, i.e. the mass of material

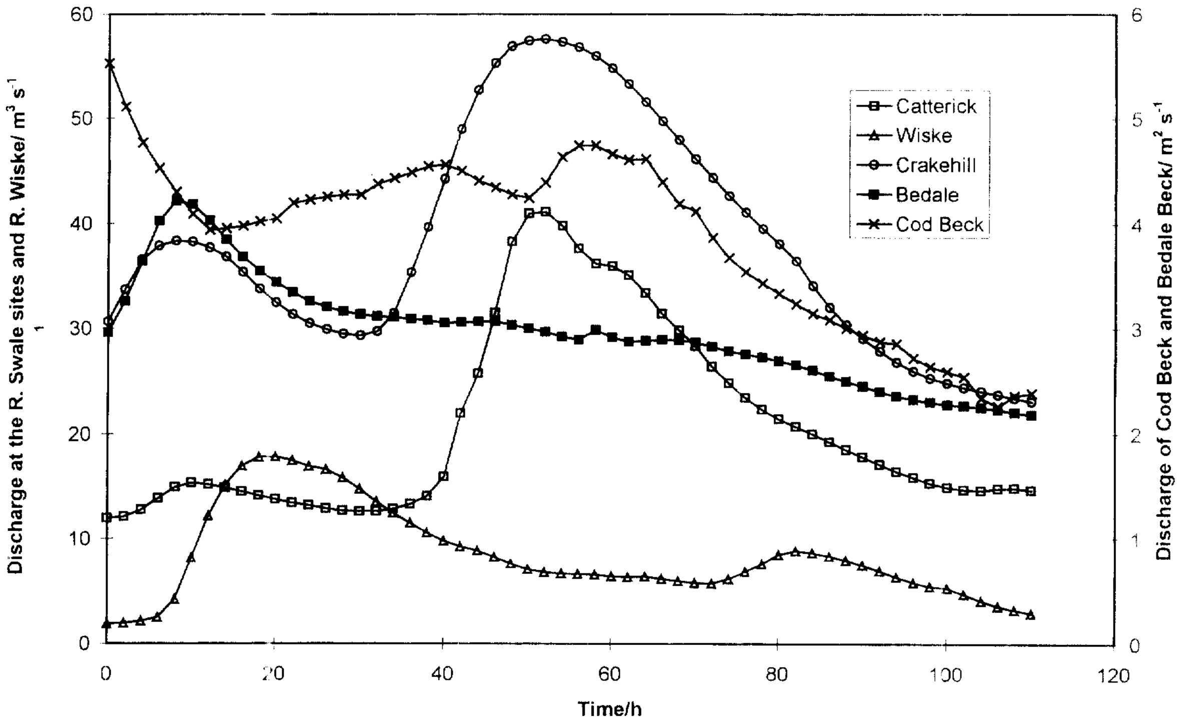


Fig. 1. Comparison of the hydrographs at the main River Swale sites and major tributaries measured on 22–26 February 1996. The discharges for the main river sites at Catterick and Crakehill as well as the River Wiske are shown on the LHS. Cod Beck and Bedale Beck water discharges are shown on the RHS (all in $m^3$ $s^{-1}$). The hydrographs have been adjusted for the transit time between the sampling stations.

in the river section is much smaller than the total throughput during the measurements.

The results of the water volume-balance are shown in Fig. 2. During the low-flow period in October, the delivery of water to the downstream site was dominated by inputs from above Catterick (hereafter called the upland or upper Swale catchment). The individual major tributaries and the minor tributaries taken together, delivered similar volumes of water. This also happened in April but with greater inputs from the upland and major tributaries and much the same contribution from the minor tributaries as measured in October. In contrast, the event in February was dominated by water delivered from the upland and River Wiske but considerable amounts from other tributaries, e.g. the minor tributaries contributed approximately 8% of the volume measured at Crakehill.

The mass-balances were calculated using Eq. (1) and Eq. (2) with $c_i = c_{i+1} = 1$ and $\Sigma_j m_{\text{net}(j)} = 0$, i.e. assuming negligible direct inputs of water or groundwater inflows/outflows.

When $M_t$ (from Eq. 1) were compared with the values calculated from the discharge data from the downstream site, reasonable agreement was found, i.e. within 7.6, 2.4 and 4.7% in October, April and February, respectively. The balance indicated slight losses in the catchment in October and April, i.e. the volume of water measured at the downstream site was slightly less than the sum of the contributions, but a slight gain in February. Considering the large size and complexity of the catchment, the water-balance is very good. It is difficult draw any concrete conclusion from the small differences observed, on the relative contributions of groundwater, direct surface or subsurface inputs not accounted for by minor or major tributaries or systematic errors in the river gauging — as approximated in Eq. (5). However,

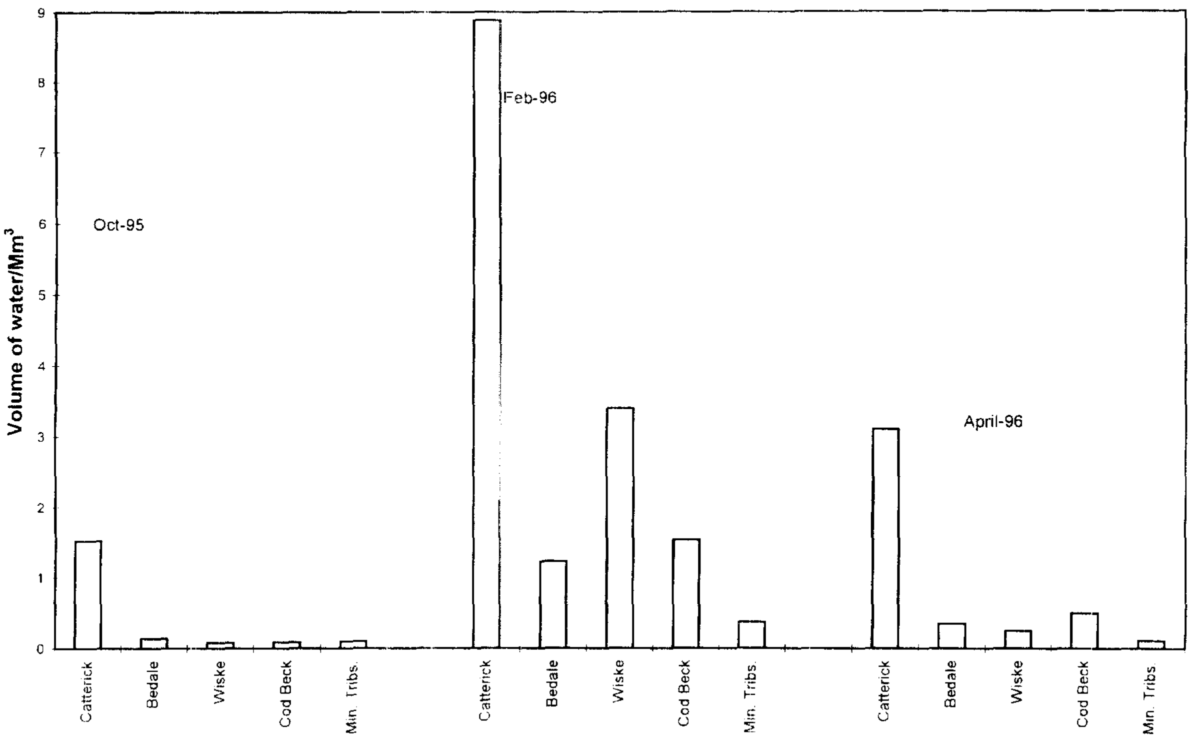


Fig. 2. Results of the water mass-balance for the three campaigns. Min. Tribs.: sum of the results from the 15 minor tributaries which were monitored daily.

the results are consistent with small groundwater effects with a greater loss of water in October after a dry summer and autumn compared with April, after a wet winter period when the groundwater table was likely to be higher.

### 5.2. Dissolved silicon and calcium

Concentrations of dissolved silicon were generally lower in the spring and autumn compared with values measured in the February campaign (House and Warwick, 1998). The various contributions to the mass-balance largely reflect the water through-put, essentially because the variations in silicon concentration along the river were much less than for other nutrients (House et al., 1997). Excellent agreement was found between the sum of the inputs from the catchment and the amount delivered to the downstream site (see Fig. 3). In October, this difference was < 0.3% of the load at Leckby gauging station, the downstream River Swale site, with a slight gain of 2.5% in April and negligible loss in February. These results indicate that interactions involving silicon, such as dissolution of mineral silica/silicates or uptake by diatoms, were not major controls on the delivery during the campaigns. This may be the result of the slow kinetics of the reactions involving silicon (House and Orr, 1992; House and Smith, 1994). This was tested by estimating release rates from bed-sediments in a fluvarium channel using sediment from traps incorporated in the bed at Leckby. With water velocities similar to those measured at low-flow in October, release rates of dissolved silicon of approximately 100 $\mu$mol m$^{-2}$ h$^{-1}$ were measured at 16°C. Using an average width for the river of 22 m (from 55 measurements of the bank to bank distance at the water line at 1-km intervals along the section) to estimate the total river bed area, the estimated increase in dissolved silicon is approximately 10 kmol during the April campaign when silicon

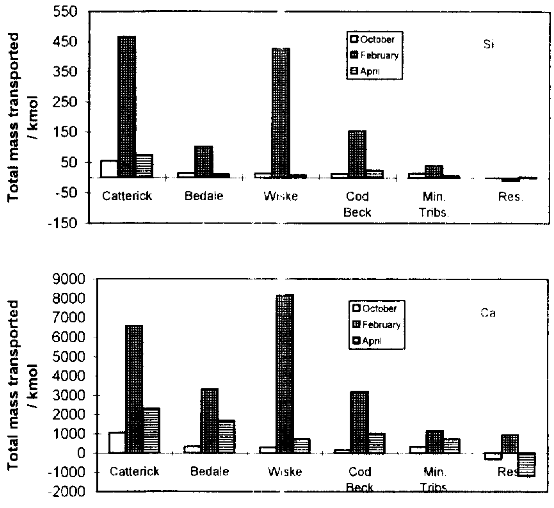


Fig. 3. Mass-balances for dissolved silicon and calcium for the three campaigns. Min. Tribs.: sum of the contributions from the 15 minor tributaries; Res.: residual of the mass-balance calculated as the difference between the load estimated at the downstream site on the River Swale and the sum of the contributions from the major and minor tributaries.

concentrations were lowest and release or dissolution most likely. The estimated silicon increase from the mass-balance (3.3 kmol) is less than calculated above — perhaps because of the effects of diatom uptake of silicon during the same period. However, considering the small difference in the mass-balances and likely systematic errors in the data, dissolved silicon must be considered to be close to dynamic equilibrium.

The mass-balance for dissolved calcium (Fig. 3), shows the importance of the harder water inflows from the major and minor tributaries to the downstream site compared with the delivery from the uplands. The residuals from the mass-balance were losses of calcium in October and April (18 and 23%, respectively) and a slight gain of 4% in February. The residuals may be viewed in conjunction with the apparent losses of water to estimate the concentration of calcium in the residual water. This leads to concentrations of calcium in the residual water of 2.3, 12.1 and 1.2 mmol dm$^{-3}$ for the October, April and February campaigns, respectively. These concentrations are within the range expected for the catchment (House et al., 1997) for October and February but much greater than expected in April. It is feasible that calcium is being lost in April as a result of calcium carbonate deposition in the lowland section — probably in association with algal biofilms (House et al., 1989; Hartley et al., 1996). Low concentrations of carbon dioxide in photosynthetically active regions of biofilms leads localised regions of high pH and large supersaturations with respect to calcite deposition as observed in the laboratory (Brady and House, 1996) and in other rivers (House and Denison, 1997). This is in agreement with the lower $CO_2$ concentrations and higher supersaturations with respect to calcite formation which were calculated for the bulk water during the measurements in April 1996 (House and Warwick, 1998).

### 5.3. Soluble and particulate phosphorus

The residuals for SRP and TDP are relatively large compared with those for dissolved silicon and calcium amounting to 53, 37 and 26% of the SRP load at the downstream site (see Fig. 4). The residuals for SRP are losses from the river water which in October and April were approximately equivalent to the inputs from the Rivers Wiske and Cod Beck. Such large differences cannot be explained in terms of losses to groundwater because the predicted concentration from the water and SRP balance are much greater than the river water concentrations measured, i.e. 27 and 48 $\mu$mol dm$^{-3}$ in October and April, respectively, compared with measured values $< 12$ $\mu$mol dm$^{-3}$. The losses in SRP are likely to be caused by net uptake of soluble phosphorus from the water by bed-sediments, macrophytes and benthic algae. The average $EPC_0$ for the surface sediment measured in the survey in June 1996 was 0.84 $\mu$mol dm$^{-3}$ (23 samples with a S.D. of 0.44 $\mu$mol dm$^{-3}$) with no discernible downstream trend in the data. Concentrations in the overlying water were considerably greater than this at low-flow (House and Warwick, 1998), approximately 6 $\mu$mol dm$^{-3}$ and therefore a net uptake of SRP by the bed-sediments is expected. This was confirmed by experiments in a fluvarium channel with sediments col-

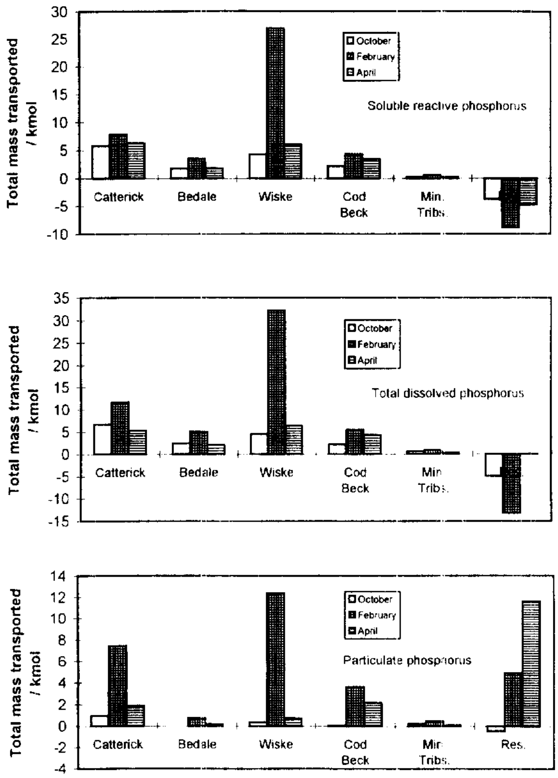


Fig. 4. Mass-balances for dissolved phosphorus and particulate phosphorus for the three campaigns. Min. Tribs.: sum of the contributions from the 15 minor tributaries; Res.: residual of the mass-balance estimated as the difference between the load delivered at the downstream site on the River Swale and the sum of the contributions from the major and minor tributaries.

Table 1
Export of SRP, TP and nitrate in the River Swale catchment and major tributaries

| Catchment/ month | SRP $kg\ km^{-2}\ d^{-1}$ | TP $kg\ km^{-2}\ d^{-1}$ | Nitrate $kg\ km^{-2}\ d^{-1}$ |
|---|---|---|---|
| River Swale[a] | 0.15 | 0.72 | 64 |
| Upper Swale[a] | 0.24 | 0.23 | 3.8 |
| River Swale | | | |
| October 1995 | 0.07 | 0.08 | 0.6 |
| February 1996 | 0.17 | 0.35 | 17.2 |
| April 1996 | 0.07 | 0.11 | 2.2 |
| Upper Swale | | | |
| October 1995 | 0.11 | 0.14 | 0.53 |
| February 1996 | 0.11 | 0.27 | 7.7 |
| April 1996 | 0.10 | 0.10 | 1.4 |
| Bedale Beck | | | |
| October 1995 | 0.12 | 0.16 | 1.4 |
| February 1996 | 0.18 | 0.29 | 19.2 |
| April 1996 | 0.10 | 0.11 | 4.1 |
| River Wiske | | | |
| October 1995 | 0.19 | 0.21 | 0.77 |
| February 1996 | 0.89 | 1.5 | 62.3 |
| April 1996 | 0.22 | 0.24 | 2.2 |
| Cod Beck | | | |
| October 1995 | 0.10 | 0.10 | 0.48 |
| February 1996 | 0.14 | 0.30 | 17.6 |
| April 1996 | 0.13 | 0.22 | 3.8 |

[a] Indicate values calculated from annual loads calculated from weekly monitoring, House et al., 1997.

lected from Leckby which showed a net uptake of SRP when the overlying SRP concentration was greater than approximately 2.5 $\mu$mol $dm^{-3}$. These fluvarium experiments indicated an uptake or release of SRP depending whether the overlying water was above or below the $EPC_0$ of the surface sediment.

In February, biological processes are at a minimum and uptake is more likely on suspended solids from river bank erosion and surface run-off from adjacent land. This is reflected in the large gain in particulate phosphorus shown in Fig. 4. Soil cores (10 cm depth, 2.5 cm diameter) from bank material at different heights above the water line collected during the survey from Maunby (NGR: SE 347 862), approximately mid-point between the two main river sites, gave $EPC_0$ values of $< 0.1$ $\mu$mol $dm^{-3}$ showing that such material will adsorb SRP when placed in contact with the river water. The results for TDP are similar to SRP except in April when there was a small gain in TDP of approximately 0.3% of the load at Crakehill. As there was a net loss of SRP during the April survey, the results are consistent with in-stream production of organophosphorus or polyphosphates compounds at this time. The mass-balances for particulate phosphorus show a net loss in October (45%) during low-flow conditions but large gains in April and February. These gains may be the result of the uptake of soluble phosphorus from the river water by suspended matter during transit downstream and the decrease in October may arise from particulate matter settling from the water in low-flow.

The balances for SRP and TP were also examined in terms of the export of nutrients from the whole River Swale catchment, the upper Swale catchment and the major tributaries. The export amounts were quantified from the mass-balance for each of the sections Eq. (2), from the catchment areas and length of the campaigns, (see Table 1). The results for the three periods were also compared with a previous report of the nutrient exports calculated from the LOIS monitoring data for 1 year with weekly measurements of nutrient concentrations (House et al., 1997). Exports of SRP are in agreement for October and April for all the catchments. The storm event generally produced greater exports for all the catchments apart from the upper Swale and Cod Beck. In contrast, the exports of TP were more variable with large increases in the storm relative to SRP and large differences between TP for the October and April campaigns for Cod Beck.

These results may be compared with total phosphorus exports from the River Swale estimated from a knowledge of the appropriate export coefficients for particular land-uses. There are a wide range of values for export coefficients available (Sharpley et al., 1995). Selected values derived from the published literature have been successfully employed by Johnes (1996) to predict exports from the River Windrush catchment, a tributary of the River Thames in the UK. The values, also adopted here, are: (all in kg $ha^{-1}$ $year^{-1}$): grassland: 0.1, cereals: 0.65, root crops:

Table 2
Land-use in the River Swale catchment

| | Upper Swale[a] $km^2$ | River Swale $km^2$ | Bedale Beck $km^2$ | River Wiske $km^2$ | Cod Beck $km^2$ |
|---|---|---|---|---|---|
| Total catchment area $km^2$ | 508 | 1457 | 142 | 216 | 217 |
| STWs: P.E./$10^3$ | 25.8 | 102.0 | 13.2 | 25.5 | 17.5 |
| Wheat | 32 | 228 | 17 | 49 | 31 |
| Winter barley | 15 | 128 | 15 | 26 | 15 |
| Spring barley | 4 | 23 | 2 | 3 | 4 |
| Total cereals | 52 | 384 | 34 | 80 | 51 |
| Potatoes | 2 | 28 | 2 | 4 | 5 |
| Sugarbeet | 0 | 18 | 0.1 | 2 | 5 |
| Horticulture | 0.1 | 1 | 0.2 | 0.1 | 0.2 |
| Beans and peas | 3 | 17 | 2 | 3 | 2 |
| Oilseed rape | 7 | 41 | 3 | 8 | 6 |
| Linseed | 0.7 | 7 | 1 | 1 | 1 |
| Total crops and fallow | 67 | 504 | 43 | 100 | 71 |
| Grassland | 138 | 429 | 54 | 81 | 47 |
| Rough grazing | 117 | 192 | 15 | 5 | 26 |
| Woodland | 4 | 16 | 2 | 3 | 2 |
| Set-aside | 2 | 8 | 1 | 1 | 1 |
| Cattle and calves/$10^3$ | 21.4 | 85.2 | 11.5 | 18.9 | 0.8 |
| Pigs/$10^3$ | 25.0 | 200.2 | 12.4 | 0 | 19.4 |
| Sheep/$10^3$ | 155.3 | 393.0 | 44.2 | 54.0 | 50.2 |
| Fowl/$10^3$ | 425.6 | 1908.7 | 49.8 | 530.2 | 429.2 |

[a]Upper Swale designates the catchment upstream of Catterick and the River Swale, the whole of the catchment to the lower sampling station near Thornton manor (NGR: SE 433 715).
STW: Sewage treatment works: P.E.: People equivalent.

Table 3
Comparison of the exports of TP estimated using export coefficients for different land-use as listed in Table 2 with the range of values measured in the three campaigns

| Catchment | Theoretical export $kg\ km^{-2}\ d^{-1}$ | Range measured $kg\ km^{-2}\ d^{-1}$ |
|---|---|---|
| Upper Swale | 0.19 | 0.10–0.27 |
| River Swale | 0.25 | 0.08–0.35 |
| Bedale beck | 0.29 | 0.11–0.29 |
| River Wiske | 0.35 | 0.21–1.5 |
| Cod Beck | 0.22 | 0.10–0.30 |

Export coefficients taken from the selection of Johnes (1996).

0.8, field vegetables: 0.65, oilseed rape: 0.65, rough grazing: 0.02, woodland: 0.02 and for livestock (all in $kg\ ha^{-1}\ year^{-1}$): cattle: 0.25, pigs: 0.07, sheep: 0.02 and poultry: 0.003 — the latter group being the lower of the values of Johnes et al. (1994). Human treated-sewage was taken as 0.38 $kg\ ha^{-1}\ year^{-1}$ (Johnes, 1996). The livestock values are slightly lower than the values adopted by Marchetti and Verna (1992). The catchment land-uses for the whole River Swale catchment, the upper Swale and the major tributary catchments, calculated using a geographic information system, are collected in Table 2.

The theoretical values shown in Table 3, are in reasonable agreement with the range measured in the three campaigns in different hydrological conditions providing confirmation that this simple approach, with a careful choice of export coefficients applicable to the region, can provide reasonable estimates of riverine loads of total phosphorus. A comparison of the predicted exports over 100 h for the whole Swale catchment compared with the upper Swale (Fig. 5), indicates that the main influences are predicted to be cattle, pigs, sheep and people with cereals important in the lower part of the catchment.

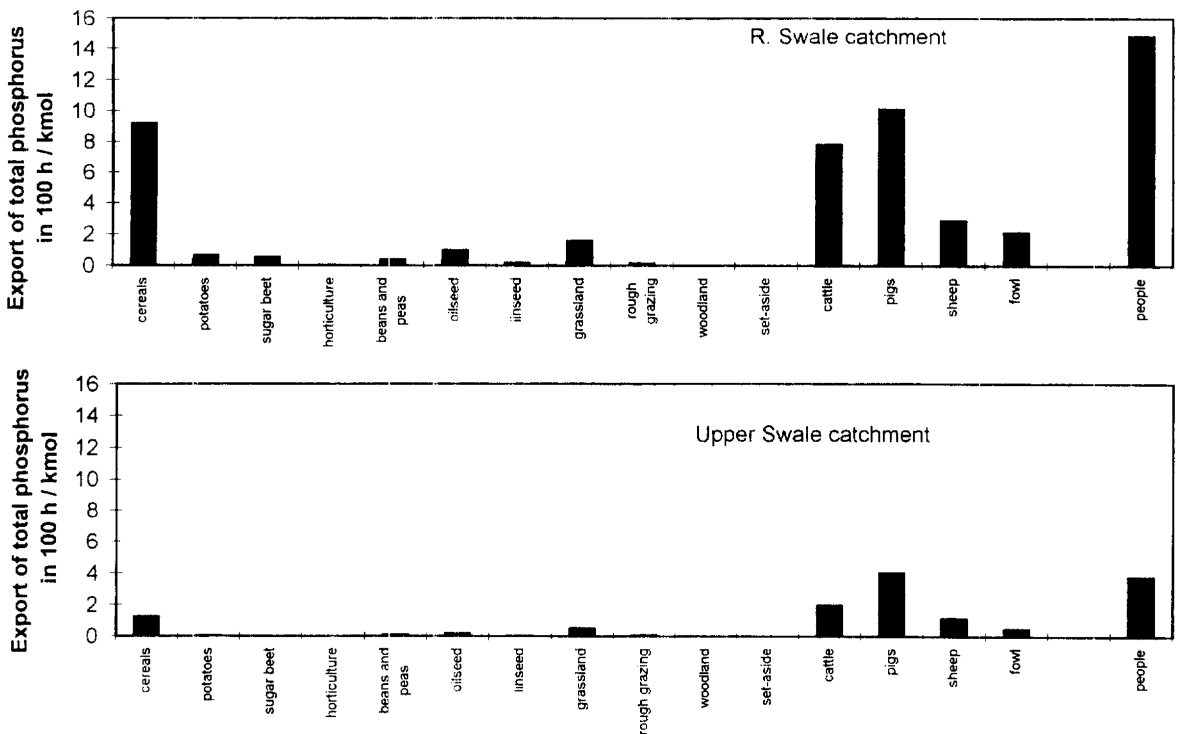


Fig. 5. Predicted exports of total phosphorus calculated for a period of 100-h (for comparison with the campaigns) for the whole River Swale catchment and the River Swale catchment upstream of Catterick (upper Swale catchment).

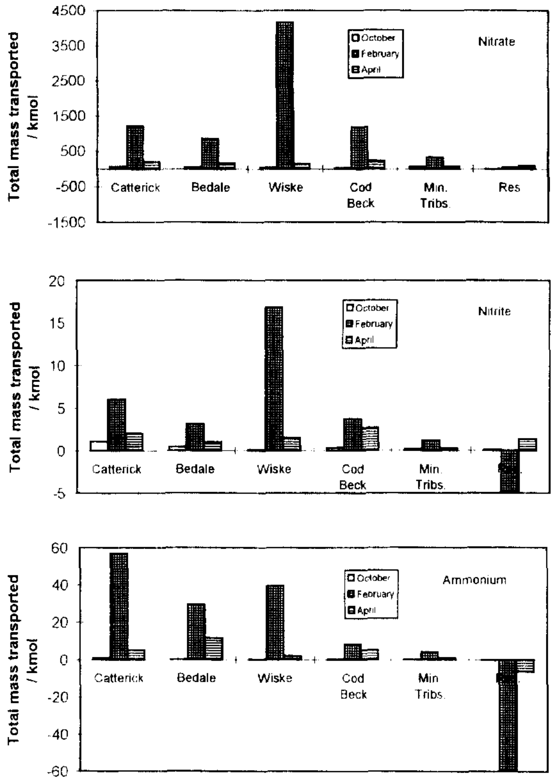


Fig. 6. Mass-balances for dissolved nitrate, nitrite and ammonium for the three campaigns. Min. Tribs.: sum of the contributions from the 15 minor tributaries; Res.: residual of the mass-balance estimated as the difference between the load delivered at the downstream site on the River Swale and the sum of the contributions from the major and minor tributaries.

### *5.4. Inorganic nitrogen compounds*

The residuals for nitrate are relatively small with a loss in October (9.9%) and gain in April (9.7%); a good balance is achieved for the data from the February storm period (0.5%). The gain in April is also accompanied by a gain in nitrite and loss in ammonium — although this is not sufficient to explain the gain in oxidised species through nitrification (Chesterikoff et al., 1992). When normalised with respect to the main river bed area, the loss of nitrate in October is equivalent to approximately 200 $\mu$mol $m^{-2}$ $h^{-1}$ which is consistent with denitrification in the bed-sediment (Pattinson et al., 1998). Large losses in ammonium were found for each of the campaigns, which were presumably caused by nitrification and adsorption to suspended material. The transformation of ammonium and nitrite to nitrate is difficult to detect because of the large nitrate loads compared with ammonium and nitrite. For example, the large loss of ammonium and smaller loss of nitrite in February, predicted from the mass-balance, totalled 64 kmol compared with a gain of 35 kmol of nitrate which is < 0.5% of the total load of nitrate delivered at Crakehill (Fig. 6).

The nitrate exports, normalised with respect to the catchment areas (Table 2), are different for the three campaigns. Very large increases in exports were found for the February storm, particularly for the River Wiske catchment. The upper Swale catchment showed the least response to storm conditions reflecting the lower intensity agriculture in the area (Table 1). Unlike the be-

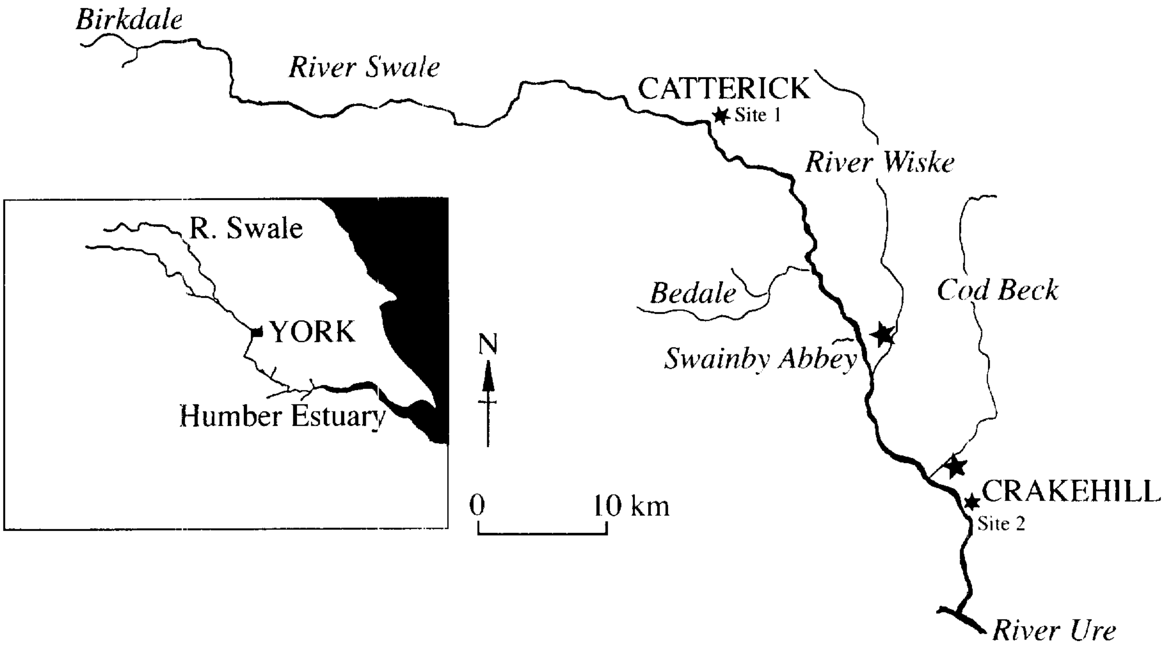


Fig. 7.

haviour of soluble phosphorus, nitrate exports were substantially greater in April during the higher river-flows compared with base-flow conditions in October. This is consistent with diffuse inputs of nitrate and mobilisation from land during rainfall events. These values are much greater than expected from annual mean exports such as those reported by Neill (1989) and Casey et al. (1993) of 1–7 and 3.1 kg km$^{-2}$ d$^{-1}$, respectively for agricultural catchments and tile-drained field plots (Bergstrom, 1987) of approximately < 1.4 kg km$^{-2}$ d$^{-1}$ for grassland and a maximum of approximately 10 kg km$^{-2}$ d$^{-1}$ for fertilised cereal plots. In contrast, the exports in the spring and autumn campaigns are close to published values for agricultural catchments and lower than the annual mean exports calculated from the LOIS weekly data and listed in Table 2.

## 6. Conclusions

The mass-balance approach enables estimates of the importance of riverine processes in the transport of chemicals in different hydrological conditions. Information about temporal changes in concentrations of solutes and particulate material alone is not sufficient to identify the effects of riverine processes without details of the kinetics and rate-determining controls on the processes. The scope of the approach is determined by the quality of the water discharge and concentration data and necessitates detailed monitoring of all inputs and outflows from the system.

The mass-balance for dissolved silicon indicated that riverine processes contribute < 10% of the total load with excellent agreement obtained between inputs and the output at the downstream site on the River Swale in a storm in February. There was some evidence, particularly in April, for losses of calcium during transit which is consist with biologically induced precipitation of calcium carbonate. The results for dissolved phosphorus show relatively large in-stream losses — possibly from the river water to bed-sediments and associated flora. There was also an indication of losses caused by sorption to suspended matter during the campaigns in April and February when the river flow was highest. Dissolved nitrate was better conserved within the system, particularly in the major storm event. There is some evidence for a net loss in October — possibly associated with denitrification and gains at the other times which may be associated with nitrification and concomitant losses in ammonium and nitrite. There is a clear indication of the loss of ammonium during all the campaigns.

The mass-balance data were also used to compare with total phosphorus loads predicted from a simple export model. Although these models are often derived from mean annual data, the predicted exports using export coefficients found applicable to other UK catchments, were found to be in the range measured in the intensive studies. Exports for nitrate were more variable than phosphorus, reflecting the greater importance of diffuse inputs.

Differences in exports were noted for all the campaigns, with very large values found for the storm event for all the catchments. Episodic events are very important in quantifying nitrate exports making the application of export coefficient models to some catchments difficult unless the coefficients are normalised with respect to rainfall intensity.

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## References

Ainsworth, A.M., Goulder, R., 1998. Microbial organic-nitrogen transformations along the Swale-Ouse river system, Northern England. Sci. Total Environ. 210/211, 329–355.

Bergstrom, L., 1987. Nitrate leaching and drainage from annual and perennial crops in tile-drained plots and lysimeters. J. Environ. Qual. 16, 11–18.

Brady, P.V., House, W.A., 1996. Surface-controlled dissolution and growth of minerals. In: Brady, P.V. (Ed.), Chemistry and Physics of Surfaces and Interfaces. Ch 4. CRC Press, Boca Raton.

Casey, H., Clarke, R.T., Smith, S.M., 1993. Increases in nitrate concentrations in the river Frome (Dorset) catchment related to changes in land use, fertilizer applications and sewage input. Chem. Ecol. 8, 105–117.

Chesterikoff, A., Garban, B., Billen, G., Poulin, M., 1992. Inorganic nitrogen dynamics in the River Seine downstream from Paris (France). Biogeochemistry 17, 147–164.

Eisenreich, S.J., Bannerman, R.T., Armstrong, D.E., 1975. A simplified phosphorus analytical technique. Environ. Lett. 9, 45–53.

Hartley, A.M., House, W.A., Leadbeater, B.S.C., Callow, M.E., 1996. The use of microelectrodes to study the precipitation of calcite upon algal biofilms. J. Colloid Interface Sci. 183, 498–505.

House, W.A., Denison, F.H., 1997. Nutrient dynamics in a lowland stream impacted by sewage effluent: Great Ouse, England. Sci. Total Environ. 205, 25–49.

House, W.A., Frickers, T., 1995. Harmonisation Programme, Land Ocean Interaction Study Newsletter, Issue Number 8, November 1995. Natural Environment Research Council, Swindon.

House, W.A., Orr, D.R., 1992. Investigation of the pH dependence of the kinetics of quartz dissolution at 25°C. J. Chem Soc. Faraday Trans 88, 233–241.

House, W.A., Smith, S., 1994. Reactions of silica in the aquatic environment. Trends Chem. Geol. 1, 53–67.

House, W.A., Warwick, M.S., 1998. Intensive measurements of nutrient dynamics in the River Swale. Sci. Total Environ. 210/211, 111–137.

House, W.A., Denison, F.H., Armitage, P.D., 1995. Comparison of the uptake of inorganic phosphorus to a suspended and stream bed-sediment. Water Res. 29, 767–781.

House, W.A., Leach, D., Warwick, M.S., Whitton, B.A., Pattinson, S.N., Ryland, G., Pinder, A., Ingram, J., Lishman, J.P., Smith, S.M., Rigg, E., Denison, F.H., 1997. Nutrient transport in the Humber rivers. Sci. Total Environ. 194/195, 303–320.

House, W.A., Shelley, N., Fox, A.M., 1989. Chemical modelling applications to experimental recirculating streams. Hydrobiologia 178, 93–112.

Jarvie, H.P., Neal, C., Robson, A.J., 1997. The geography of the Humber catchment. Sci. Total Environ. 194/195, 87–100.

Jarvie, H.P., Whitton, B.A., Neal, C., 1998. Nitrogen and phosphorus in the east coast British rivers: Speciation, sources and biological significance. Sci. Total Environ. 210/211, 79–109.

Johnes, P.J., 1996. Evaluation and management of the impact of land use change on the nitrogen and phosphorus load delivered to surface waters: the export coefficient modelling approach. J. Hydrol. 183, 323–349.

Johnes, P.J., Moss, B., Phillips, G., 1994. Lakes — Classification and Monitoring: A Strategy for the Classification of Lakes/R and D Note 253. National Rivers Authority, Bristol, UK.

Ladle, M., Baker, J.H., Casey, H., Farr, I.S., 1997. Preliminary results from a recirculating experimental system: observations of interactions between chalk stream water and inorganic sediment. In: Golterman, H.L. (Ed.), Interactions Between Sediments and Freshwater. Junk, The Hague, pp. 252–257.

Leeks, G.J.L., Jarvie, H., 1998. The LOIS programme. Sci. Total Environ. 210/211, 5–20.

Lewis, D.R., Williams, R.J., Whitehead, P.G., 1997. Quality simulations along rivers (QUASAR): an application to the Yorkshire Ouse. Sci. Total Environ. 194/195, 399–418.

MAFF, 1992. Small Area Statistics from June 1992 Agricultural Census. MAFF Central Laboratories, York.

Marchetti, R., Verna, N., 1992. Quantification of the phosphorus and nitrogen loads in the minor rivers of the Emilia-Romagna coast (Italy). A methodological study of the use of theoretical coefficients in calculating loads. Sci. Total Environ. Suppl. 1992, 315–336.

Mitchell, G.C., 1994. System design for field tests in flowing waters: design and use of outdoor artificial streams in ecotoxicology. In: Hill, I.R., Haeimbach, F., Leeuwangh, P., Matthiessen, P. (Eds.), Freshwater Field Tests for Hazard Assessment of Chemicals. Ch 7. CRC Press, Ann Abor, pp. 127–139.

Murphy, J., Riley, J.P., 1962. A modified single solution method for the determination of phosphate in naturalwaters. Anal. Chim. Acta. 27, 31–36.

Neill, M., 1989. Nitrate concentrations in river waters in the south-east of Ireland and their relationship with agricultural practice. Water Res. 23, 1339–1355.

Pattinson, S.N., García-Ruiz, R., Whitton, B.A., 1998. Spatial and seasonal variation in denitrification in the Swale-Ouse system, a river continuum. Sci. Total Environ. 210/211, 289–305.

Sharpley, A.N., Hedley, M.J., Sibbesen, E., Hillbricht-Ilkowska, A., House, W.A., Ryszkowski, L., 1995. Phosphorus transfers from terrestrial to aquatic ecosystems. In: Tiessen, H. (Ed.), Phosphorus in the Global Environment. SCOPE 54, Ch 11. John Wiley.

Vogel, A.I., 1961. A Text Book of Quantitative Inorganic Analysis, 3rd ed. Longmans, pp. 436–437.

Zhmud, B.V., House, W.A., Denison, F.H., 1997. Release kinetics and concentration profile of dissolved silicon in compacted sediments. J. Chem Soc. Faraday Trans. I 93, 3473–3478.